

CONTACT POTENTIAL DIFFERENCES AS MODIFIED
BY GASEOUS ATMOSPHERES

by

John MacDonald Barstow
B. S. Washburn College, 1923

and

Floyd Lester Nutting
B. S. in M. E. University of Kansas, 1915

Submitted to the Department
of PHYSICS and the
Faculty of the Graduate School
of the University of Kansas
in partial fulfillment of the
requirements for the degree of
Master of science

Approved by:

F. E. Kester
Head of Department

June 13, 1924

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BIBLIOGRAPHY

1. Gray, Andrew, A Treatise on Electricity and Magnetism
pp. 440-456
2. Lehfeldt, Electro-Chemistry. Part 1, General Theory
p. 159
3. Fournier, E. E., The Electron Theory. Chapter 6
4. Spiers, Frederick, Contact Electricity. Phil. Magazine.
Vol. 49. Art. 4 1900. pp. 70-90
5. Millikan, R. A., Einstein's Photoelectric Equation and
Contact Electromotive Force. Physical Review. Vol. 7,
1916. pp. 18-32
6. Millikan, R. A., A Direct Photoelectric Determination
of Planck's "h". Phys. Rev. Vol. 7, 1916. pp. 355-388

PURPOSE

The purpose of this research was to find out, if possible, the effect on the contact potential difference of two metals, of immersion of one of them in different gases.

HISTORY

It has long been known that if two dissimilar metals such as say zinc and copper are brought into contact and then separated, each acquires a charge, in this case, the copper negative and the zinc positive. The real reason for this acquisition of charge by dissimilar metals has been the object of much controversy. For some time, it was held that there was an actual difference of potential between the metals of such a value that when they were brought into contact, electricity flowed in such a direction as would bring the two metals to a state of equipotential and that the amount of electricity which flowed from one metal to the other could be measured by the charge acquired by them.

This explanation of the action of two dissimilar metals on contact has served very well up until comparatively recently. Many experiments were performed to show the existence of such Pds. First among these were the experiments of Volta, which showed that such a Pd. existed but did not evaluate it. The first evaluation of the contact Pd. was made by Kohlrausch¹ in 1851, who arranged a pair of plates of dissimilar metals so

¹ Gray--A Treatise on Electricity and Magnetism. pp. 448-450

that they formed a condenser. The metals were brought close together, connected metallically for a moment and then this connection broken and the plates separated, one being connected to the ground and the other being brought into contact with the indicator of a Dellman electrometer. The deflection of the electrometer was noted and then the operation was repeated with a Daniell cell interposed between the plates in the connecting wire. In this way, the contact Pd. was evaluated, knowing the e.m.f. of the cell.

In all of these early experiments, the Pds. of the metals were of course always measured in air. A little later a series of experiments were made by Clifton of Oxford (1876) and Ayrton and Perry¹ in which the contact Pds. between metals and solutions were measured. From their experiments, the e.m.f. of a Daniell cell was calculated by addition of the contact potentials of the substances in contact. The results are as follows:

Daniell Cell

Substances in contact	Pd. (volts)
Copper and saturated CuSO_4 solution	.070
Saturated CuSO_4 and saturated ZnSO_4 solutions	.095
Saturated ZnSO_4 and zinc	.430
Zinc and copper	.750
Total	1.155
Observed	1.10

This calculated Pd., though surprisingly close to the actual Pd., must be said, in the light of the present day knowledge of single electrode potentials, to be somewhat in error. For example, it is known now that the Pd. of copper against a saturated solution of copper sulfate is in the neighborhood

of .6 volt while the results above show it to be only .070 volt.

Pellat in 1881 made a long series of tests on metals, using the balancing method of measurement, previously designed and used on some unpublished researches by Lord Kelvin. The method consisted of making two parallel plates of dissimilar metals the plates of a condenser and balancing a known variable potential against the potential of contact so that when the plates were separated, one being connected to the ground and the other to the indicator of an electrometer, there would be no deflection of the electrometer. In other words, the potential was adjusted until the condenser formed by the plates of dissimilar metals had no charge because the plates were at the same potential.

The materials of which the connecting wires are made in such a method is immaterial, because, in any series of metallic conductors, all e.m.f.'s due to contact cancel out except the contact e.m.f. of the end materials. In equation form, denoting the contact potential between two metals by the vinculum interposed between them, this may be expressed as follows:

$$\text{Cu/Pt} + \text{Pt/Ag} + \text{Ag/Zn} = \text{Cu/Zn}$$

Pellat's measurements, all of which were made in air, checked this rule to within experimental error. He made attempts at measuring contact Pds. in different gases, but his results indicated that as long as no chemical action took place, the contact potentials remained practically the same. As far as is known, he made no attempt to remove the air film from the surfaces of the metals, so that no results would be

expected.

The presence of gas films on the surfaces of metals was fully recognized in a research performed by Mr. Frederick Spiers in 1899. The results of this research were published in the Philosophical Magazine for January, 1900. He used the balance method of measurement and evidently succeeded in removing some of the surface gas films by heating at very low pressures.

His apparatus consisted of a long and rather narrow glass tube in which his two metal plates (also long and rather narrow) were suspended lengthwise. By tilting the tube at the correct angle, the plates could be made to hang very close together and the movable plate was brought away from the other by means of a small electro-magnet placed outside of the tube. Part of the time this movable plate was of iron, allowing the magnet to attract it alone, but when the movable plate was aluminum, a piece of iron was fastened to its back in order to use the magnet. Nothing was said as to whether magnetism in the iron altered the contact Pds. or not. Heating of the metals was accomplished by applying two Bunsen flames to the whole system, glass, plates and all. This rather awkward application of heat to be sure helped in evacuation of the tube and there is little doubt but that it removed part of the surface film yet it seems that the probability of its accomplishing the desired result would not be very great. Also a glass surface is not an extremely good electrostatic insulator and his insulation was totally effected by glass. He was troubled somewhat with oxidation of aluminum and iron which he was balancing against

platinum. In one case he attributed a contact potential of zero between iron and platinum to the fact that the iron had a coating of oxide over it, saying that oxidation always causes contact activity of metals to disappear.

In Millikan's work on the Einstein photoelectric equation² he was forced to measure contact potentials between a faraday cylinder of copper oxide and freshly cut lithium and sodium surfaces. He found the contact Pds. to be real and fairly constant, showing that oxidation does not reduce the contact activity of a metal to any very marked degree.

DESCRIPTION OF APPARATUS

Since it was evident in the light of past experiments that the medium in which the metal was immersed did have something to do with the contact Pd. if the surface films could be removed, our apparatus was designed to remove as completely as possible any such film. We thought it also desirable to determine the effect of change of atmosphere on one of the metals alone, leaving the other in its previous condition. The only obstacle in the way of realization of such a scheme was the question as to whether a dielectric interposed between the two dissimilar metals would alter in any way the contact Pd. To determine this, a short preliminary research was carried out. Copper and zinc were used as the dissimilar metals. The Pd. between them was first measured in air with nothing placed between the plates. The original setup is given diagrammatically in Figure 1. The zinc tends to lose electrons

2 Phys. Rev. Vol. 7 No. 1 p. 18 1916

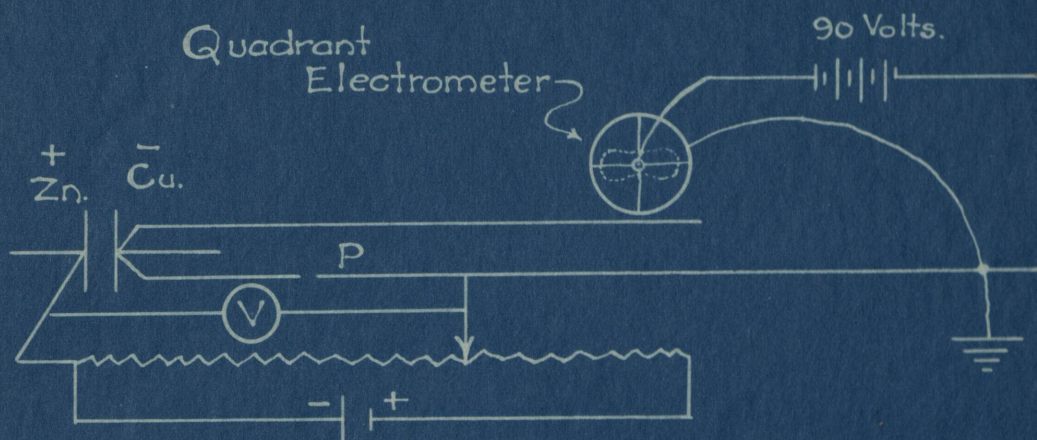


Fig I . Diagram of Original Set up.

to the copper. This tendency is balanced by the counter e.m.f. of the potentiometer, so that, when the contact points are separated at P and the condenser plates separated by moving the grounded copper plate, there is no deflection on the electrometer. The reading of the voltmeter gives the contact potential directly.

The whole apparatus was inclosed in a wire cage measuring 30 inches on each edge and built of bare metal fly screen stretched over a light wooden frame. It was found that this would eliminate inductive charges from without and annoying electrostatic influences. This screen was set on a stone pier and securely soldered to a ground wire. Inside were placed the metal plates, 3 dry cells, potentiometer, two contact points, quadrant electrometer, with its high potential battery, and slide for movable plate.

The values of the Pds. measured between the zinc and copper plates varied from .58 volt to .9 volt, depending on whether the surfaces of the metals were left untouched or were cleaned by rubbing with fine emery cloth and wiping clean with cheese cloth. Immediately after cleaning in this way the Pd. was .9 volt.

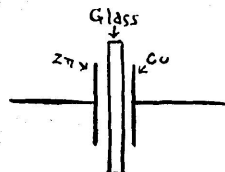
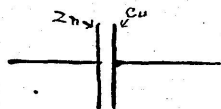
In about three hours it had dropped to

.82 volt.

After three days it registered steadily

.60 volt.

When the contact Pd. had reached this steady value, a thin piece of glass was interposed between the two plates. The Pd. in this case varied from 0 to 2 volts, depending evidently upon the condition of the glass.

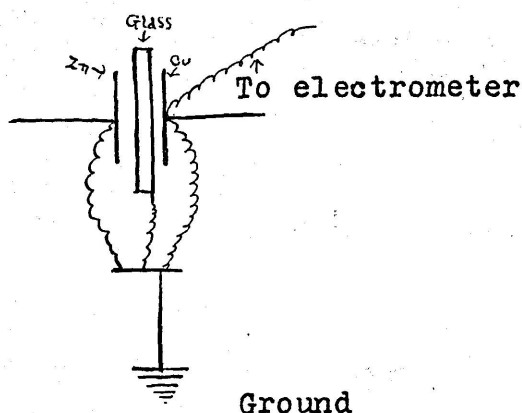


Before glass was inserted After glass was inserted

This was attributed to charges which might have been resident on the glass due to handling or rubbing against some other material. In order to determine definitely whether or not charges on the glass were responsible for the variations of the Pd. measured, a piece of copper wire was inserted between the glass and its hard rubber support and the other end grounded. Then a flame was played lightly over the surface of the glass. These two things were done in order to remove all charges from the surface of the glass. There is little doubt but that this was accomplished and that the plate was brought to zero potential (relative) as far as its position would allow it to be brought to such a potential. But the contact potential now registered from 1.34 volts to 2 volts. Upon removing the glass the Pd. would immediately drop back to .6 volt. After giving the situation some serious thought, it was concluded that the false value for the contact Pd. obtained with glass interposed was due to the fact that when the air was ionized in the neighborhood of the glass plate, the negative potential applied to the zinc plate (which was left applied continuously) caused the glass plate to take on a positive charge sufficient to balance the attraction of the negative charge on the zinc plate for it. Then enough more potential would have to be applied to the zinc to overbalance the contact potential against the copper, because the copper,

on being brought close to the positively charged and now insulated glass plate, would take on a negative charge on being earthed. Thus the whole system would be in equilibrium, with the value of the negative potential applied to the zinc as the new zero. The total therefore would be greater than the real contact potential by the amount that was on the zinc when the air around the glass plate was ionized.

To obviate this difficulty, the copper, glass and zinc were all grounded when the flame was applied to the glass.



The ground connection to the glass plate was broken first, then the zinc ground connection was broken and a negative potential applied to it. The copper ground connection was then broken and the copper plate which was connected to the insulated quadrants of a Dolezalek quadrant electrometer was drawn away, decreasing the capacity of the condenser. With this method of procedure, the contact P.d. again was found to be in the neighborhood of .6 volt. It was therefore concluded that the interposition of a dielectric did not alter the contact P.d. between two metals in air, provided it had been reduced to zero (ground) potential first and then well insulated from both the metal plates.

There was one thing which rather hindered the use of glass and that was the fact that it reduced very markedly the sensitivity of the condenser method because it separated the plates so far. This reduction of sensitivity could be eliminated or at least substantially lessened by the use of some material whose dielectric constant was greater than that of glass. With this end in view, different metals were interposed in place of the glass, the same precautions being observed as to grounding as before. In every case the sensitivity was increased very greatly over the glass and the contact potential of the copper and zinc in question measured easily to .01 volt.

It simply remained then to arrange the parallel plates so that one could be held in some sort of a container which could be evacuated and refilled with a gas and the other placed outside of the container with the insulated piece of metal forming that part of the boundary of the container between the two. A method for outgassing the metal in the container also had to be provided for. These specifications were combined in the following plan.

A Woulfe flask was decided upon as the container for the metal to be tested because of its three openings at one end, two of which could be used for inserting the supports for the metal while the third could be used for pumping. The bottom of the flask was cut off and the edge ground smooth so that a plate of brass could be sealed upon it with sealing wax. The metal was a piece of platinum foil, 2" x 4" x $\frac{1}{1000}$ ". It was gold soldered with an electric arc welder to heavy copper

leads which were to be used as supports for it in the flask. These leads were turned down slightly at the ends where the foil was soldered to them and bent at right angles as shown in Figure 2. After the foil was soldered to the leads it was wrapped around each lead once which reduced its effective area to 2" x 2.5". This was necessary for three reasons: First to bring the corners of the foil farther away from the sides of the flask, thus insuring clearance of the sealing wax at the point of seal between the glass and the brass plate which was to form the bottom of the flask, second, to insure uniform heating throughout the foil on passage of an electric current through it, and third, to expose only platinum on the surface which was to be one plate of the condenser.

The platinum foil and leads, when ready, were inserted into the flask, the leads being up through the outside holes of the flask and fastened in place by tight fitting tapering cork stoppers fitted over them and pushed tightly up into the necks. Both leads were then sealed inside and out with Bank of England sealing wax, after they had been adjusted so that the surface of the foil was about 1mm. from the bottom edge of the flask and was as level as possible. The heavy brass plate was then sealed on to the bottom of the flask, also with Bank of England sealing wax, by slowly heating the plate with a ring of wax on it and seating the flask (which had also been warmed) on it, pressing it down firmly.

By means of a 110 - 3 volt A. C. transformer with a controlling rheostat placed in the high tension side, 100 amperes could be sent through the platinum foil which was placed in the

low tension side of the transformer; sufficient to heat the foil to a white heat. On account of the danger of melting the wax, heating frequently to a red heat for a short time was resorted to instead. The amount of current necessary to heat the foil to red and white heats was determined before it was placed in the flask. 40 amperes D. C. sent through it heated it only so that it felt warm to the touch. The particular piece of foil in hand contained a trace of irridium. The wax seals on the copper leads served to make the flask gas tight and at the same time insulated the leads from the glass electrostatically. When assembled, the stretched platinum foil was just below the brass plate, parallel to it and about one-sixteenth inch from it. Figure 3 shows the container in detail.

Into the middle neck of the flask a length of pyrex tubing, 10 mm in diameter and with charcoal bulb attached was sealed in the same manner as the copper leads. Through this, gases were introduced and pumped out. The charcoal was used to remove any water vapor that might not have been taken up by the calcium chloride vessel on the intake line and also to help evacuate the flask. On exhausting or removing gases from the flask, the charcoal was heated with an asbestos covered electric heater. For vacuum it was then cooled with an iced salt water solution in a Dewar flask. For gases it was allowed to slowly cool to room temperature during the run. A short piece of wire was sealed into the tube about 8 inches from where it entered the flask. The purpose of this sealed-in wire was to test the vacuum obtained by an electric dis-

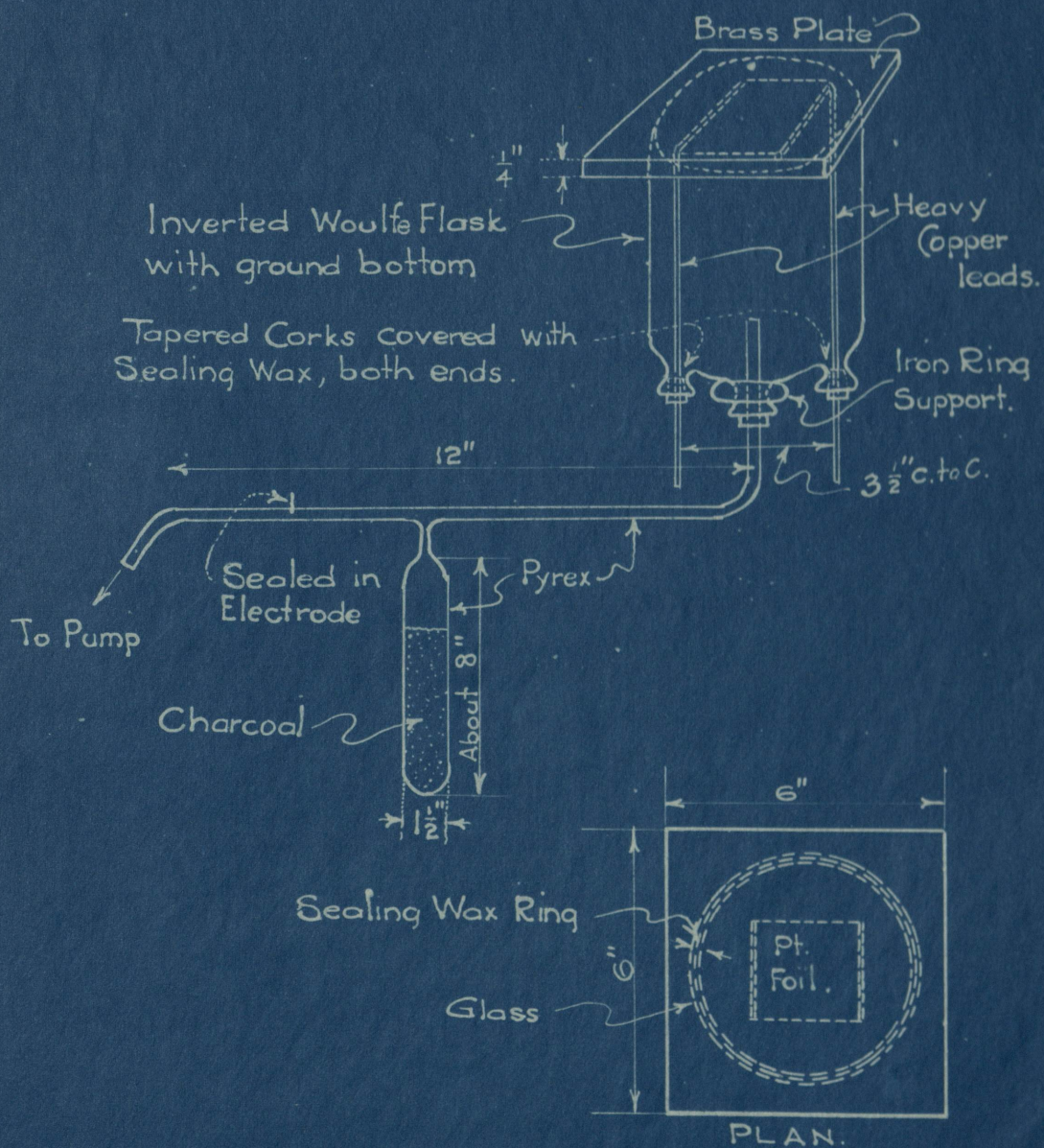


Fig. III Detail of Container.

charge.

The high voltage battery was the water cell type and consisted of pairs of bent copper zinc strips soldered together. There were 100 cells in series but because of shorting and other e.m.f. losses, the voltage measured only 90 volts. It was used to maintain a high potential on the vane of the electrometer. The potentiometer was a slide wire rheostat, (72 ohms - 3 amps.) across which three dry cells in series were connected.

The electrometer, which was a very good one, was the quadrant type, made by Pye & Co., Cambridge, England.

The contact points used were the standard type; hard rubber insulating base on top of which was screwed a small metal cup or container for the mercury. Above, a suspended platinum point dipped into the mercury.

The pump used was a "Hyvac" pump made by the Central Scientific Co.

As in the preliminary experiment, all the apparatus except the pump and the voltmeter was put inside of the screen cage. Silk threads attached to the contact points served to raise the small platinum wires out of the mercury and thus break contact. The potentiometer was regulated by means of stronger cords stretched from the sliding contact in either direction along the resistance coil and out through opposite faces of the cage, so that the contact could be pulled either way at will by an operator outside of the cage.

SPECIAL PROBLEMS IN OPERATION

Trouble was experienced from the first in arranging the wires that were moved when the movable plate was moved in such a manner that they moved a minimum distance with respect to any other conductor in the system. Of course, any two wires in the system at different potentials formed a condenser whose capacity changed as the wires moved. This trouble was especially noticed in connection with the conductor between the movable plate and the insulated quadrants, because near this wire was the high potential lead from the positive terminal of the 90 volt battery to the vane of the electrometer. In the first arrangement of the apparatus, these two wires ran parallel to each other for about four inches. When the plate was moved the wire connecting it and the insulated quadrants moved with respect to the high potential wire about an eighth of an inch, which gave a deflection of about 5 cm. on the scale. When this wire was placed so that it moved away from instead of towards the high potential wire, the deflection was of the same magnitude in the opposite direction. To eliminate this difficulty, this wire was turned at right angles to the high potential wire and fastened permanently to the mercury cup on top of the hard rubber post on the contact points and another connection was made between this point and the movable plate. This last mentioned connection was effected by the use of three wires as shown in Figure 4. The wire leading from the plate and the wire leading from the contact points were both of rather large gauge and not very flexible. These two stiff wires were connected by a finer

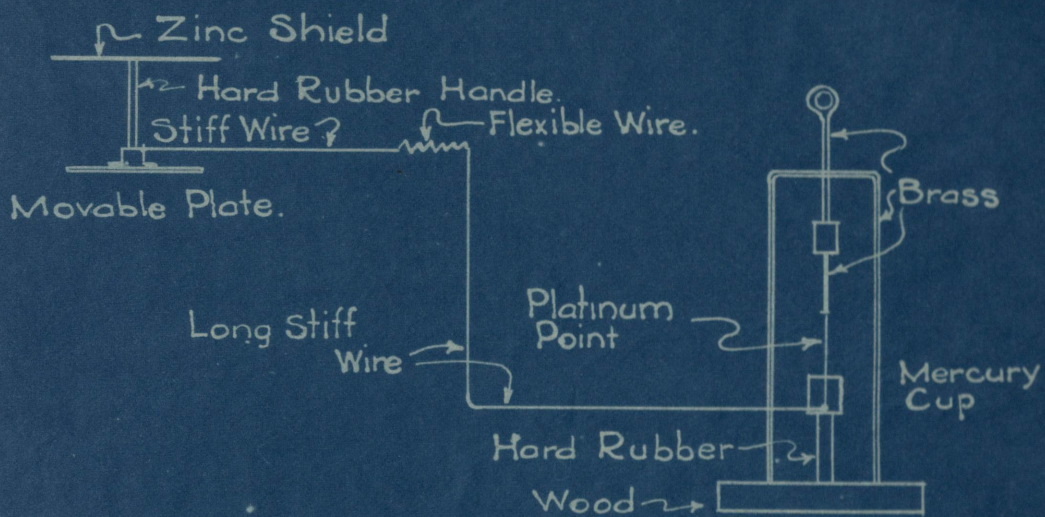


Fig. IV. Contact Points and Wire Connections.

flexible wire which allowed an inch or two of motion between the two. This allowed motion of the plate with very little motion of any wire with respect to any other wire near it.

A zinc shield was placed above the movable plate and on the same support so that it moved up and down with the plate. It was grounded by metallic contact with the screen. This shield prevented the possibility of there being any condenser action between the plate and the top of the cage as it was moved towards it or away from it.

Another obstacle that was encountered was that of making the wax-copper seal gas tight. When both wax and copper were hot the seal was gas tight but when both cooled, the copper evidently shrunk away from the wax, leaving a gas passage between the two. This was rather effectually stopped by drawing the wax out over the surface of the copper for a considerable distance from the seal in a very thin layer so that there was very little offset where the end of the wax surface met the copper surface. With this arrangement, fair vacuums were attained and held for several hours.

The system was tested for electrostatic leaks between the brass plate and the copper leads and practically none were found to exist.

The introduction of the various gases was effected by means of a three-way stop-cock inserted between the pump and the charcoal bulb.

OPERATION, RESULTS AND CONCLUSION

The results here given were all taken with zinc as the movable plate and platinum as the fixed plate. Both the sur-

faces were rubbed with crocus paper and allowed to stand several days in the atmosphere so that they were in a fairly stable condition as far as potential difference was concerned.

The flask was first exhausted in order to be sure that a fairly good vacuum was attainable. While the pump was going the charcoal bulb was heated to drive off some of the occluded gases in it. When it was evident that the condition of the seals and the charcoal would produce a good vacuum, the pump was stopped, the stop-cock opened and air was allowed to enter, bringing the flask back to the same condition as that before the pump was started. The Platinum had not been outglowed. after standing one hour in order to assure equilibrium conditions the contact Pd. was measured and found to be

.98 volt (zinc pos. to platinum)

Immediately after taking this measurement the pump was started and the charcoal bulb heated. In about 20 minutes, when the pump had become quiet, the charcoal bulb was immersed in an iced salt water solution the temperature of which was about -10°C . The platinum foil was outglowed 6 times at intervals of about 3 minutes. Each time it was heated to a light red heat and held in this condition for 15 or 20 seconds. With this treatment the contact Pd. rose to

1.07 volts

or nearly .1 volt more than it was in air. The vacuum obtained was estimated to be about 1 mm by the nature of a discharge sent through the flask using the brass plate as one electrode and the sealed in electrode on the intake line as the other. The discharge showed striations and was of a very

light lavender color, almost transparent. For a period of one hour at least after this discharge, no measurements could be taken as a result of charges which had been left on the inside of the glass container and on the wax. The above Pd. was measured about 3 minutes after the last outglowing of the foil but before the charge was sent through. It indicates rather decisively that the removal of the surface of film had been accomplished and that the difference between the pds. was a direct result of this removal.

Next, the flask was washed out several times with hydrogen by means of the three-way stop-cock. Between the hydrogen cylinder and the stop-cock was a calcium chloride drying tube used to dry the hydrogen thoroughly before it entered the flask. Finally the flask was filled with hydrogen and the contact Pd. measured. It was

1.08 volts

During the washings with hydrogen the platinum foil was outglowed several times. There seemed to be a small rise in the potential difference. The charcoal bulb had not been heated, and it was thought that perhaps the hydrogen was displacing some of the occluded gases in it. The pump was therefore started again and the charcoal heated for about $\frac{1}{2}$ hour and then allowed to cool to room temperature while the flask was washed with hydrogen several times again and the platinum outglowed 5 times more. The Pd. then was measured in hydrogen. It was found to be

1.10 volts

This was one hour after the first hydrogen had been let

in. In order to see if the effect was due to slow absorption the flask was left full of hydrogen for 5 hours. The Pd. then measured

1.10 volts

It was allowed to stand 19 hours longer. The Pd. then measured

1.11 volts

A little more hydrogen was let in to make up for that which the charcoal had occluded and the Pd. again measured. It was found to be still

1.11 volts

The pump was started again and the hydrogen pumped out of the flask. The flask was then washed out several times with oxygen, the platinum being heated 6 times at intervals as before. The charcoal bulb was also heated strongly for about 15 minutes and allowed to cool to room temperature in the oxygen atmosphere. The Pd. in the oxygen atmosphere about 20 minutes after the first oxygen had been let in was

1.00 volt

The flask was evacuated again and washed out 4 times more with oxygen, the platinum being outglowed each time. At the end of 40 minutes of such treatment, the Pd. was still

1.00 volt

Three and one-half hours later the Pd. was

.98 volt

The pump was then started again and the flask evacuated. The charcoal was heated strongly for 15 minutes and then cooled in an iced salt solution. The platinum was outglowed six times. At the end of the process the Pd. in the vacuum

measured again

1.07 volts

This was an exact check on the former result obtained in a vacuum. It will also be noticed that the result obtained in oxygen was the same as the result obtained in air, showing that the oxygen in the air produced the same effect upon the surface of the platinum as the pure oxygen atmosphere.

In order to satisfy ourselves that our results were correct, the whole process was repeated. Hydrogen was again admitted in the same manner as before, i.e. with outglowing of platinum and heating and cooling of the charcoal. In one hour the Pd. measured

1.11 volts

Three hours later it measured

1.11 volts

Oxygen was then admitted and the Pd. fell to

1.01 volts

Twenty-three hours later it still measured

1.01 volts

This was considerable of a discrepancy from the former value of .98 volt but might have been due to two things. (1) Heating the platinum so vigorously might have smoothed its surface some. It was observed in the preliminary experiment on zinc and copper that any roughing up of metallic surfaces made the metal appear more positive and it is reasonable to believe that smoothing would have the opposite effect. (2) Heating the copper leads continuously with a gas flame deposited a thin coating of carbon on the wax coverings near the

seal which was distinctly visible toward the last of the experiment. This no doubt caused a small electrostatic leak between the brass plate and the copper leads.

The oxygen was finally removed and air allowed to enter, the platinum being glowed and the charcoal heated and allowed to cool as before. In one hour the Pd. in air registered

1.01 volts

a check on the preceding value for oxygen.

Before zinc had been decided upon as the movable plate of the system several tests similar to those described above were made with nickel as the movable plate. While the results show qualitatively the same effect of the vacuum and hydrogen on the platinum, the whole system at that time showed unmistakable signs of electrostatic leaks. Tests made across the insulators confirmed the conclusion. Quantitatively therefore, these results would be somewhat in error and are therefore not given. The nickel also seemed to behave rather erratically. In fact, once the indications seemed to show that even if the leaks were allowed for, the Pd. between the two changed in sign, i.e. the nickel became for a short time negative to the platinum. At this time it was taken out and polished with fine emery cloth, and upon being put back, it was found that it had regained its positive potential with respect to the platinum.

One thing that was found to be essential to the proper working of the apparatus was that the copper leads be warmed occasionally; enough to feel warm to the touch. At times, especially after the apparatus had stood for a considerable

length of time at the temperature of the room, the first attempts at balancing the contact P.d. between the two metals would result in values much higher than the values obtained on previous occasions. If then a flame were applied to the copper leads long enough for them to absorb sufficient heat to feel warm to the touch, the contact P.d. would drop to its former value almost immediately. No certain explanation for this peculiar phenomenon could be found, but the following may be offered.

When the copper leads were sealed with wax, the glass and copper were both warmed up to the temperature of the melted wax, or thereabouts. When the system cooled, the copper, having a greater coefficient of expansion than the glass and wax, shrunk away from the wax, leaving a very minute space between the two surfaces. At first, before the wax was drawn down over the copper, as explained before in this discussion, this shrinkage amounted to enough to cause considerable of a gas leak. In this case, when the wax and copper were warmed the leak would stop, which located the leak conclusively at the junction. The two surfaces so close together could be considered as a condenser which would take a charge when a positive potential was placed upon the copper. Any charge thus placed upon the wax far up on the inside of the sleeve which covered the copper would be hard to remove by an ordinary method such as playing a flame over its exposed surface. But if the copper could be made to expand and fill up the space, the charge would be conducted off. At least, the observed results would lead one to believe that such was

the case. At such times, a brief playing of the flame over the surface of the wax was not effective.

The results of this bit of research seem to confirm the growing tendency of observers to believe that the so called contact potential between dissimilar metals is in part at least a function of the gas or substance in which the metal is immersed. They further indicate that the potential of platinum immersed in hydrogen is about .1 volt more negative than the potential of platinum in the air, since there is no reason to believe that the zinc plate had anything whatever to do with the consistent changes observed in the contact Pd. Mr. Spiers³ refers to an article of Lord Kelvin's wherein it is said that Lord Kelvin made the observation that a platinum plate soaked in hydrogen was temporarily .1 volt positive to another platinum plate not so treated. Our results mean just the opposite of this statement. Although Spiers intimated that his results confirmed Lord Kelvin's statement, it is hard to see how he substantiates his claim, as in his apparatus, both aluminum and platinum were immersed in hydrogen so that the effect of such an atmosphere on either alone would be hard to determine.

Again, since platinum does not oxidize at all readily, and does not combine chemically with hydrogen, the metal itself probably remained the same throughout the entire process, the atmosphere in which it was immersed only changing. This eliminated any possibility of the changes in Pd. being

3. Phil. Mag. Vol. 49 Art. 4, p. 82.

due to oxides or any other chemical combination of metal and gas.

Although the vacuum was only fair, it is very likely that the very definite change of the contact Pd. observed with the platinum in it was due to the fact that the surface film had at least been temporarily removed by the outglowing. It seemed rather odd that the platinum should be more negative in hydrogen than in a vacuum, and indeed this may not have been true. The Pd. measured in the vacuum obtained may have been and no doubt was due in part at least to the little bit of gas remaining in the flask, though readings were taken as soon as possible after the last outglowing. However, we think the results in oxygen and hydrogen may be taken as accurate to at least .01 volt.

All the potential difference measurements were taken with a Sieman-Halske voltmeter, three volt scale.

From the point of view of electro-chemistry it may be interesting to note that the Pd. measured with the platinum immersed in hydrogen gave just the potential difference that might be calculated for the potential difference that would exist between oxygen and hydrogen electrodes immersed in a solution normal with respect to the hydrogen ion (1.12 volt). On the other hand, when oxygen was admitted and the platinum was soaked with oxygen the Pd. did not even begin to approach anything like a zero value, which apparently ought to follow if the effect is due to the hydrogen electrode. Along this line of reasoning it is evident that nothing definite may be said except that the change from the oxygen to the hydrogen

was accompanied by a change toward the negative of the potential of the platinum foil.

The conclusions that may be drawn from this work may be briefly summed as follows:

- (1) The gas in which a metal is immersed has a definite effect on its contact potential with any other metal.
- (2) Platinum is more negative as determined from its contact potential, in a vacuum than in air.
- (3) Platinum is about .1 volt more negative in hydrogen than in oxygen, as determined from its contact potential.

In concluding this article, we wish to thank all who have helped us in this work and especially Dr. F. E. Kester for his aid in making apparatus, for his many helpful suggestions and for the interest he has taken in the work. We wish also to thank Dr. Cady for his suggestions and for supplying the hydrogen needed in the tests that were made.

Blake Hall,
June 13, 1924

J. MacD. Barstow
F. L. Nutting

